

## ANTIFOULING COATING

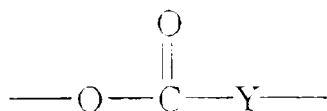
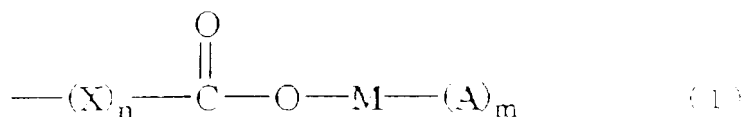
## BACKGROUND ART

The present invention relates to an antifouling coating  
5 comprising a metal-containing acrylic resin.

## BACKGROUND ART

Ships, piers and other underwater structures or  
equipment tend to attract aquatic organisms such as barnacles,  
10 mussels, and algae which interfere with an efficient operation  
of ships and cause a waste of fuel in ships or other means  
and shorten the service life of piers etc. To prevent such  
attachment of life to underwater structures, it is common  
practice to coat the surfaces of the structures with an  
15 antifouling coating. As a representative antifouling coating  
heretofore in use, there is a matrix type antifouling coating  
comprising a formulation of a resin and a vinyl or alkyd resin  
which is insoluble in seawater. However, since a coating of  
this type releases an antifouling ingredient together with the  
20 resin into the seawater, a long-term stable antifouling effect  
cannot be expected and, moreover, since the insoluble resin  
remains on the surface of the film and is peeled off at times, the  
coating has the disadvantage that particularly when it is  
applied to ships, the resistance between the seawater and the  
25 coating surface is increased to slow down the speed of ships.

In recent years, in view of the long-term stable antifouling  
effect and the advantage of low toxicity, antifouling coatings  
have been utilized widely and, as the result, a coating  
comprising a metal-containing acrylic resin composition has been  
30 proposed. It has been known that such a composition is not  
only antifouling but also resistant to salt water and that the  
metal-containing acrylic resin has been reported to be  
particularly effective in the prevention of attachment of algae  
and barnacles. However, the metal-containing acrylic resin  
35 composition is not so effective as the metal-containing acrylic  
resin composition of the present invention.



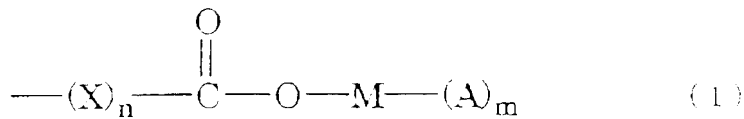
residue derived from a hydroxy acid,

wherein  $n$  represents an integer greater than or equal to 1,  $m$  represents an integer greater than or equal to 1,  $X$  represents a radical derived from a hydroxy acid, and  $A$  represents a radical derived from a hydroxy acid.

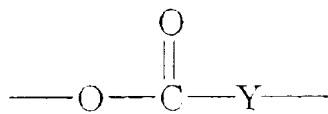
5 The present invention relates to a polymer of the above-described formula (1) having a content of acid more than 4% by weight.

The present invention relates, in a secondary aspect, to a method of producing a polymer of the above-described formula (1).

10 The present invention relates to a method of producing a polymer of the above-described formula (1), which method comprises the steps of: (a) reacting a hydroxy acid with a hydroxy acid derivative to form a polymer of the above-described formula (1);



wherein  $X$  represents a radical of the formula:



15 wherein  $Y$  represents a radical derived from a hydroxy acid;  $M$  represents a radical;  $n$  represents an integer greater than or equal to 1;  $m$  represents an integer greater than or equal to 1;  $A$  represents a radical derived from a hydroxy acid, and  $X$  represents a radical derived from a hydroxy acid.

20 The present invention relates to a method of producing a polymer of the above-described formula (1), which method comprises the steps of: (a) reacting a hydroxy acid with a hydroxy acid derivative to form a polymer of the above-described formula (1);

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention is now described in detail.

25 The present invention relates to a method of producing a polymer of the above-described formula (1), which method comprises the steps of: (a) reacting a hydroxy acid with a hydroxy acid derivative to form a polymer of the above-described formula (1); (b) reacting the polymer of the above-described formula (1) with a hydroxy acid derivative to form a polymer of the above-described formula (1);





5

10

20

30

35









average degree of polymerization in the range 1.0 to 1.5. When the polymerization degree is less than 1, the film-forming properties are insufficient to form films with satisfactory properties in certain instances. When it exceeds 1, the thickness of the film increases very rapidly with the polymerization degree and the films can be obtained at times.

The average degree of polymerization must be 1.0 or more to obtain films of polyethylene glycol- $\alpha$ -methyl styrene copolymer which will have satisfactory properties. The polymerization degree of the copolymer with a theoretical degree of polymerization 1.0 is 1.0 to 1.5.

The metal-containing copolymer can be added to conventional additives including oil and antifoulant to provide an antifouling coating. This antifouling coating is a water-soluble antifouling coating having self-polishing properties.

The second aspect of the invention is directed to an antifouling coating comprising a metal-containing copolymer resin having at least the group of the above formula (I) in a film thickness of 0.001 to 0.1 cm. The resin contains a solvent-soluble antifouling agent. The preferred degree of polymerization of the copolymer is 1.0 to 1.5. If the degree is less than 1.0, the resin may be more difficult to form and the properties may be inferior. The resin may be formed by a method such as the following: (a) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (b) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (c) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (d) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (e) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (f) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (g) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (h) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (i) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (j) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (k) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (l) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (m) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (n) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (o) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (p) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (q) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (r) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (s) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (t) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (u) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (v) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (w) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (x) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (y) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (z) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation.

The resin may be formed by a method such as the following: (a) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (b) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (c) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (d) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (e) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (f) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (g) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (h) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (i) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (j) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (k) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (l) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (m) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (n) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (o) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (p) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (q) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (r) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (s) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (t) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (u) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (v) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (w) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (x) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (y) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation; (z) a solution of the copolymer resin in a solvent is applied to a substrate and the solvent is removed by evaporation.





10

15

25

35













5

10

20

30





5

10

15

20

25

650











In run 8, the reaction was carried out in the same manner as in Example 1, but with an initial amount of 10.1 wt. %.

5 Example 9

In preparation of metal-containing acrylic resin, varnish 14

The same reaction vessel as used in Example 1 was charged with 1.0 parts of varnish 14, 0.1 parts of copper acetate and 0.1 parts of hydroquinone monomethyl ether (MTHQ) and the reaction was carried out in the same manner as in Example 1, but with an initial amount of 10.1 wt. %.

10

In run 10, Example 10

15

In preparation of metal-containing acrylic resin, varnish 14

The same reaction vessel as used in Example 1 was charged with 1.0 parts of varnish 14, 0.1 parts of copper acetate and 0.1 parts of hydroquinone monomethyl ether (MTHQ) and the reaction was carried out in the same manner as in Example 1, but with an initial amount of 10.1 wt. %.

20

In run 11, Example 11

In preparation of metal-containing acrylic resin, varnish 14

25

The same reaction vessel as used in Example 1 was charged with 1.0 parts of varnish 14, 0.1 parts of copper acetate and 0.1 parts of hydroquinone monomethyl ether (MTHQ) and the reaction was carried out in the same manner as in Example 1, but with an initial amount of 10.1 wt. %.

30

In run 12, Example 12

In preparation of metal-containing acrylic resin, varnish 14

The same reaction vessel as used in Example 1 was charged with 1.0 parts of varnish 14, 0.1 parts of copper acetate and 0.1 parts of hydroquinone monomethyl ether (MTHQ) and the reaction was carried out in the same manner as in Example 1, but with an initial amount of 10.1 wt. %.

35

reaction and 0.1 parts of copper powder were used. The value for  $\eta_{inh}$  of the reaction was higher than in Example 1. The reaction was carried out with a nonvolatile fraction of 4.1 wt. %.

5

#### Preparation Example 17

Preparation of metal-containing acrylic resin (varnish 17)  
The same reaction vessel as used in Preparation Example 16 was charged with 1 part of methylol, 0.1 parts of copper powder and 0.1 parts of azobisisobutyronitrile (AIBN), and 100 ml of  $\gamma$ -butyrolactone (BGL) was added. The reaction was carried out in otherwise the same manner as in Example 16 to give varnish 17 with a nonvolatile fraction of 4.1 wt. %.

10

15

#### Preparation Example 18

Preparation of metal-containing acrylic resin (varnish 18)  
The same reaction vessel as used in Preparation Example 16 was charged with 1 part of methylol, 0.1 parts of copper powder and 0.1 parts of azobisisobutyronitrile (AIBN), and the reaction was carried out in otherwise the same manner as in Example 16 to give varnish 18 with a nonvolatile fraction of 4.1 wt. %.

20

#### Preparation Example 19

Preparation of metal-containing acrylic resin (varnish 19)  
The same reaction vessel as used in Preparation Example 16 was charged with 1 part of methylol, 0.1 parts of copper powder and 0.1 parts of azobisisobutyronitrile (AIBN), and 100 ml of  $\gamma$ -butyrolactone (BGL) was added. The reaction was carried out in otherwise the same manner as in Example 16 to give varnish 19 with a nonvolatile fraction of 4.1 wt. %.

25

30

#### Preparation Example 20

Preparation of metal-containing acrylic resin (varnish 20)  
The same reaction vessel as used in Preparation Example 16 was charged with 1 part of methylol, 0.1 parts of copper powder and 0.1 parts of azobisisobutyronitrile (AIBN), and 100 ml of  $\gamma$ -butyrolactone (BGL) was added. The reaction was carried out in otherwise the same manner as in Example 16 to give varnish 20 with a nonvolatile fraction of 4.1 wt. %.

35

are given in Table 1. The results of the reaction of the  
 100% of the monomer with the monomer as in Example 1 are  
 given in Table 1. With a 100% of the monomer as in Example 1.

##### 5 Example 1. Preparation of a polymer.

The same reaction mixture as described in Example 1 was  
 prepared with the same monomer as in Example 1. The reaction  
 mixture was prepared with the same monomer as in Example 1. The  
 reaction mixture was prepared with the same monomer as in Example 1.  
 10 The reaction mixture was prepared with the same monomer as in Example 1.

##### Example 2 and Comparative Examples 4 and 5

The reaction mixture as described in Example 1 was prepared  
 15 with the same monomer as in Example 1. The reaction mixture was prepared with the same monomer as in Example 1. The reaction mixture was prepared with the same monomer as in Example 1.

The reaction mixture as described in Example 1 was prepared  
 25 with the same monomer as in Example 1. The reaction mixture was prepared with the same monomer as in Example 1. The reaction mixture was prepared with the same monomer as in Example 1.

Example 3: The reaction mixture as described in Example 1 was prepared  
 30 with the same monomer as in Example 1. The reaction mixture was prepared with the same monomer as in Example 1. The reaction mixture was prepared with the same monomer as in Example 1.

Antes de la guerra, el gobierno de la nación

Antes de la guerra, el gobierno de la nación

Antes de la guerra, el gobierno de la nación

Antes de la guerra, el gobierno de la nación

5 Antes de la guerra, el gobierno de la nación

Antes de la guerra, el gobierno de la nación

Antes de la guerra, el gobierno de la nación

Antes de la guerra, el gobierno de la nación

Antes de la guerra, el gobierno de la nación

10 Antes de la guerra, el gobierno de la nación

Antes de la guerra, el gobierno de la nación

Antes de la guerra, el gobierno de la nación

Antes de la guerra, el gobierno de la nación

Table 10

Unit weight parts	Example																Compar. Ex.		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Varnish 1	40	45												25	25				
Varnish 18			45	40	40									20	25				
Varnish 20						45										20			
Varnish 21						40	45										25		
Varnish 22								25											
Varnish 23									20										
Varnish 24										40									
Varnish 25											45								
Varnish 26												20					40		
Varnish 27													15				40		
Varnish 28																		40	
Varnish 29																			40
Copper suboxide	20	25	25	20		5		20		25	30		20	20	20		15	25	25
Copper rhodanide				20		20	15	20		20						30	20	15	
Zinc bloom	5		5		15	5		5			2	10	5	5	5		10	5	5
Titanium dioxide				2	2			2		2		2				2	2	2	
Anthracyanine blue					2	2		2		2		2				2	2	2	
FeO		2	2		2					2		2				2	2	2	2
Red iron oxide	2	2	2	2		2		2		2	2		2	2	2		2	2	2
Pyrrhione zinc	2				5	2		5				5			2			2	2
Pyrrhione copper		2	2						5	5			2						
Tetramethylthiuram disulfide						2													
Antifoulant 1	2				2		4										2		
Antifoulant 2		2													2				
Antifoulant 3				4															2
Antifoulant 4				2												4			2
Antifoulant 5			2														5		
Antifoulant 6		2					5		2	5									
Antifoulant 7						4										2		2	
Antifoulant 8			2															2	
Antifoulant 9							5												2
Antifoulant 10		2															2		
Antifoulant 11						2										2			
Antifoulant 12									2								2		
Antifoulant 13								2										2	
Antifoulant 14									2									2	
Antifoulant 15			2					2					2		2				
Antifoulant 16					5	2		5				2							
Antifoulant 17														4			4		
Antifoulant 18			2					2								2			
Antifoulant 19																	2		
Polyvinyl ether		2	2	2			5	2	2	2		5	2			5	5	5	5
Chlorinated paraffin	2			4			4	2	2	4			4			4	4	4	4
Dibutyl sebacate		2					2								2				2
Sumi resin	5				5						2		2				5	5	5
Talc resin																			
Wood resin						4									2				
Hydrogenated palm resin									2							2			
Diisobutylated resin																			4
Hydrogenated tall oil resin																			
Resin ester		2												2			2		
Copper naphthenate																	5		
Sumi resin																	5		
Hydrogenated tall oil resin																			
Resin ester																			
Antifoulant 20																			
Antifoulant 21																			
Antifoulant 22																			
Antifoulant 23																			
Antifoulant 24																			
Antifoulant 25																			
Antifoulant 26																			
Antifoulant 27																			
Antifoulant 28																			
Antifoulant 29																			
Antifoulant 30																			
Antifoulant 31																			
Antifoulant 32																			
Antifoulant 33																			
Antifoulant 34																			
Antifoulant 35																			
Antifoulant 36																			
Antifoulant 37																			
Antifoulant 38																			
Antifoulant 39																			
Antifoulant 40																			
Antifoulant 41																			
Antifoulant 42																			
Antifoulant 43																			
Antifoulant 44																			
Antifoulant 45																			
Antifoulant 46																			
Antifoulant 47																			
Antifoulant 48																			
Antifoulant 49																			
Antifoulant 50																			
Antifoulant 51																			
Antifoulant 52																			
Antifoulant 53																			
Antifoulant 54																			
Antifoulant 55																			
Antifoulant 56																			
Antifoulant 57																			
Antifoulant 58																			
Antifoulant 59																			
Antifoulant 60																			
Antifoulant 61																			
Antifoulant 62																			
Antifoulant 63																			
Antifoulant 64																			
Antifoulant 65																			
Antifoulant 66																			
Antifoulant 67																			
Antifoulant 68																			
Antifoulant 69																			
Antifoulant 70																			
Antifoulant 71																			
Antifoulant 72																			
Antifoulant 73																			
Antifoulant 74																			
Antifoulant 75																			
Antifoulant 76																			
Antifoulant 77																			
Antifoulant 78																			
Antifoulant 79																			
Antifoulant 80																			
Antifoulant 81																			
Antifoulant 82																			
Antifoulant 83																			
Antifoulant 84																			
Antifoulant 85																			
Antifoulant 86																			
Antifoulant 87																			
Antifoulant 88																			





Table 3

	I sample																Compar I *						
	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	4	5	6	7	
0 months	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
12 months	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
16 months	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
22 months	0	0	0	0	0	0	0	0	0	0	0	5	0	0	0	0	0	0	15	10	5	20	
24 months	0	0	0	0	0	0	0	0	0	0	0	10	5	5	0	0	0	0	50	50	50	60	
Condition from 0 to 24 months	Normal																Cracked		normal		Cracked		Slightly cracked

The following is a list of the names of the persons who  
 were present at the meeting held on the 1st day of  
 January, 1900, at the residence of Mr. J. H. Smith,  
 at the corner of Main and Second Streets, in the  
 city of New York.

5      Mr. J. H. Smith, President.